

INFRARED SPECTROSCOPIC AND ESCA STUDIES ON DINITROGEN
COMPLEXES OF SOME TRANSITION METALS

by

Börje Folkesson

Lund 1973

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av

Börje Folkesson

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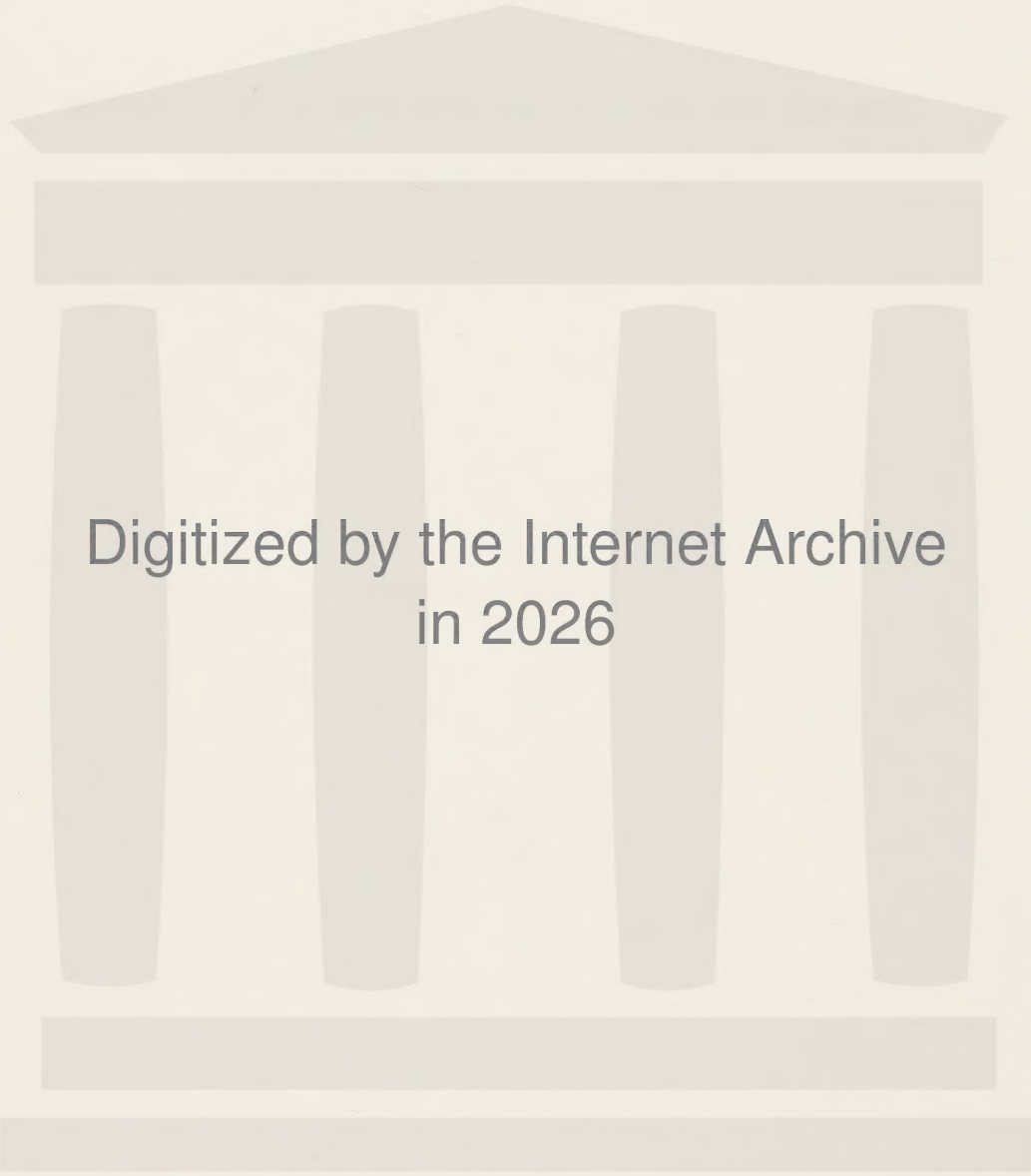
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This review summarizes the results of the following papers.

- I. Folkesson, B. Infrared Absorption Intensities of the N-N and M-N₂ Stretching Vibrations in Ruthenium and Osmium Dinitrogen Complexes Acta Chem. Scand. 26 (1972) 4008.
- II. Folkesson, B. The Influence of Anions on the Infrared Absorption Intensity of the N-N Stretching Vibration in Some Ruthenium and Osmium Dinitrogen Complexes Acta Chem. Scand. 26 (1972) 4101.
- III. Folkesson, B. On the Decomposition of the Dinitrogenpentammine-osmium(II) Ion in Aqueous Solutions Acta Chem. Scand. 26 (1972) 4157.
- IV. Folkesson, B. On the Infrared Absorption Intensity of the N-N Stretching Vibration in Some Iridium and Rhenium Dinitrogen Complexes Acta Chem. Scand. 27 (1973) 276.
- V. Folkesson, B. ESCA Studies on the Charge Distribution in Some Dinitrogen Complexes of Rhenium, Iridium, Ruthenium and Osmium Acta Chem. Scand. 27 (1973) 287.
- VI. Folkesson, B. On the Polarity of the Dinitrogen Ligand in a Dinitrogen Complex of Iron Acta Chem. Scand. submitted for publication.

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Abbreviations used in the text

X	= Halogen, unless otherwise stated
Ph	= Phenyl group
Me	= Methyl group
Ar	= Aryl group
R	= Alkyl group
M	= Metal
L	= Ligand
diphos	= Bis(1,2-diphenylphosphino)ethane
dte	= Diethyldithiocarbamate
DMSO	= Dimethylsulfoxide
DMF	= Dimethylformamide
CNDO	= Complete neglect of differential overlap
SCF MO	= Self-consistent field molecular-orbital
μ	= Dipole moment
μ_{red}	= Reduced mass

1. INTRODUCTION

One of the more fascinating fields of inorganic chemistry today is that of the reactions and properties of complexes of molecular nitrogen with transition metals. Interest in this field is not localized just to the preparation of new compounds but spans both biochemical and industrial aspects. It is now possible that a model for nitrogenase, the dinitrogen fixing enzyme in certain microorganisms, can be found. From this knowledge one can perceive the construction of an analogous synthetic compound and thus it may be possible that more economical methods will become available for the production of nitrogenous fertilizers. The problem facing chemists is the abundance of dinitrogen in our atmosphere and its extreme chemical inertness. Because of this inertness the methods of fixing dinitrogen are expensive and demand high temperature and pressure. It was, therefore, of considerable interest when in 1965 the first dinitrogen complex of a transition metal, $\text{Ru}(\text{NH}_3)_5\text{N}_2\text{X}_2$ ($\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{BF}_4^-, \text{PF}_6^-$), was reported by Allen and Senoff.¹ This was not the first time that attempts had been made to fix dinitrogen using transition metals. Fixation of dinitrogen by mixed systems composed of transition metal compounds and organometallic compounds has been reported by Vol'pin and Shur,² but at that time no stable dinitrogen complex had been isolated from the mixed systems. The work of van Tamelen³⁻⁴ is also of great importance in this connection. Both groups have successfully achieved cyclic processes for preparing ammonia in yields which established e.g. titanium as a catalytic partner in the reaction scheme. It is, however, not so easy to reduce coordinated dinitrogen when it is in a stable complex. Several early attempts to reduce coordinated dinitrogen

in some complexes of the Allen type have been performed.⁵⁻⁷ These investigations show that the dinitrogen ligand is neither reduced to ammonia by common reducing agents nor affected by protonation of strong acids. It must, however, be pointed out that hydrazine and ammonia have been obtained by the reduction of some unstable binuclear dinitrogen complexes.⁸⁻⁹ Recently, it has been found¹⁰ that dinitrogen in $\text{CoHN}_2(\text{PPh}_3)_3$ could be reduced in the presence of compounds of other transition metals. This reduction results in measurable amounts of ammonia. This is the first example where dinitrogen has been reduced when it is in a stable complex. Further investigations that might be of importance concerning the conversion of dinitrogen to ammonia are the protonation reactions recently performed by Chatt et al.¹¹⁻¹² They find that dinitrogen is protonated in bisdinitrogen-molybdenum and -tungsten complexes during their reactions with some acid chlorides. Furthermore, these bisdinitrogen complexes give, on treatment with hydrogen chloride or bromide, an N_2H_2 complex. Although this N_2H_2 complex has not yet been reduced to ammonia, its formation is probably important in understanding the function of nitrogenase.

There is thus an intense activity in the field of dinitrogen fixation to transition metals, both in the preparation of new complexes and in their properties and reactions. Soon after the discovery of the first dinitrogen transition metal complex,¹ complexes of osmium,^{13,14} cobalt,¹⁵ iridium¹⁶ and rhenium¹⁷ with dinitrogen were also prepared. The first direct indication that the complexes contain dinitrogen bound to metal is found in the infrared spectrum, which shows an absorption band in the region $2\,200 - 1\,900\text{ cm}^{-1}$, the exact position being dependent on the metal to which N_2 is bonded. This band has

been assigned to the N-N stretching frequency (ν_{NN}) of coordinated N_2 . The marked shift in ν_{NN} from the free N_2 ($2\,331\text{ cm}^{-1}$)¹⁸ indicates a disturbance of the dinitrogen molecule and thereby a decrease in the N-N bond order. This is caused by a σ -bond to the metal and by π -back donation from filled metal d-orbitals into antibonding π -orbitals of N_2 . The intensity of the N-N stretching vibration absorption implies that the N_2 is in an unsymmetrical environment, coordinated at one end rather than in a symmetrical π -bond configuration. This conclusion is also confirmed by X-ray crystallographic studies on a ruthenium^{19,20} and a cobalt^{21,22} dinitrogen complex, which show the M-N-N entity to be linear.

The present investigation was started to increase knowledge about bonding and polarity of the N-N bond in the dinitrogen complexes. Infrared absorption intensities are known²³ to be related to the charge distribution and its change with interatomic distance in a molecule. By means of ESCA²⁴ the effective charges on atoms in a molecule can be determined. It is thus possible to determine the degree of "activation" of the dinitrogen bound to metal by these kinds of measurements. This has been realized by other scientists as well and after the present investigation was started there have appeared some reports²⁵⁻²⁷ dealing with infrared intensity measurements on dinitrogen complexes. These investigations have demonstrated the utility of infrared intensity measurements in assessing the π -electronic delocalization in some transition metal dinitrogen complexes. It has also been found^{25,26} that more meaningful conclusions about the π^* -acceptor ability of the dinitrogen ligand can be obtained from intensity measurements than in any other of the earlier investigations²⁸⁻³⁰ based only on frequency data. Furthermore, from

the qualitative relationship between ν_{NN} and absolute intensity it has been proposed²⁷ that the infrared intensity of the N-N stretching vibration is largely determined by the extent of π -electronic charge transferred from the transition metal to the dinitrogen ligand during the N-N stretching vibration. Also ESCA measurements³¹ have been performed on some dinitrogen complexes of rhenium. The presence of two N1s electron peaks in the spectrum indicates²⁴ different effective charges on the nitrogen atoms. It was thus shown that the N-N bond has an appreciable polarity.

The present investigation deals with infrared spectroscopic and ESCA measurements on the following dinitrogen complexes:

$\text{Ru}(\text{NH}_3)_5\text{N}_2\text{X}_2$, $\text{Os}(\text{NH}_3)_5\text{N}_2\text{X}_2$, where $\text{X} = \text{Cl}$, Br and I ; $\text{IrClN}_2(\text{PPh}_3)_2$, $\text{IrClN}_2(\text{C}_8\text{H}_{12}\text{O}_4)(\text{PPh}_3)_2$, $\text{FeH}_2\text{N}_2(\text{PPh}_3)_3$ and the following rhenium dinitrogen complexes: $\text{ReClN}_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2$, $\text{ReClN}_2[\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2]_2$, $\text{ReClN}_2(\text{Ph}_2\text{PCH=CHPPh}_2)_2$, $\text{ReClN}_2(\text{PMe}_2\text{Ph})_4$ and $\text{ReClN}_2(\text{PPh}_2\text{Me})_4$.

Before the measurements and results on these complexes are presented, a more general description of dinitrogen complexes is given.

2. GENERAL DESCRIPTION OF DINITROGEN COMPLEXES

In this chapter only a short review of dinitrogen complexes and their properties is given. For a more detailed description the reader is referred to some of the reviews, e.g. Ref. 32 and 33, which have been published recently.

2.1 Transition metals and ligands.

The transition metals that form stable dinitrogen complexes are mainly members of Groups VIII and VII of the periodic system. Quite recently, however, evidence for dinitrogen complexes of molybdenum³⁴ and tungsten³⁵ have been reported. The oxidation states of the metal atoms forming stable complexes are low and are those normally considered as being stabilized by good π -acceptor ligands. Anomalous in this respect are the dinitrogen complexes of ruthenium(II) and osmium(II) with ammonia as the other ligand. In fact, the dinitrogen considerably stabilizes the bivalent oxidation state in these complexes.^{36,37} The metal d-electron configurations most often found are d^6 and d^8 . Almost all known dinitrogen complexes are diamagnetic, indicating complete spin coupling. Since dinitrogen can be considered as a ligand analogous to carbon monoxide, it is not surprising that the oxidation states of the metal atoms are low and that the metals lie mainly to the right in the transition metal series. Both these conditions lead to metal atoms with high d-electron configurations capable of participating in $M \rightarrow L$ π -bonding, which later will be shown to be important in the stabilization of dinitrogen complexes.

For most dinitrogen phosphino complexes the other ligands are either halide or hydride ions. It is well known that most transition metal hydride complexes have strong π -acceptor ligands coordinated as well. It could be that the correct balance of hydride and π -acceptor ligands places a metal ion in a favourable state to coordinate dinitrogen. Since dinitrogen probably bonds to a metal ion mainly through a $M-N_2$ π -bond, the favourable state may be where the hydride (or halide) puts sufficient negative charge on the metal

that the metal readily forms a $M-N_2$ π -bond. These observations suggest the metal, oxidation state and type of ligand to use when attempting to prepare dinitrogen complexes.

2.2 Preparation of dinitrogen complexes.

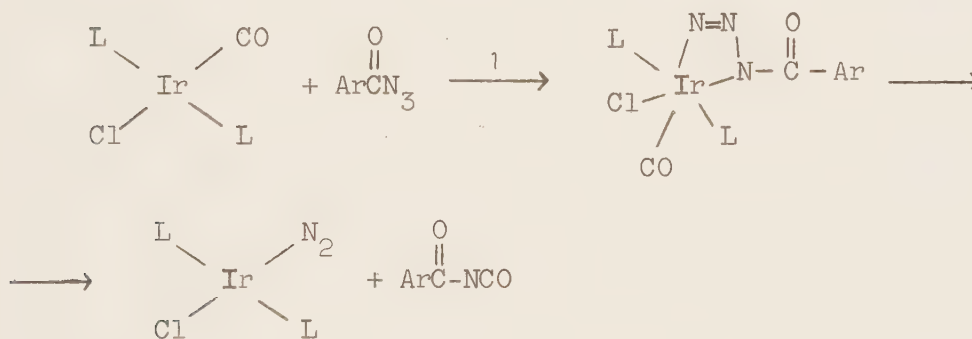
The methods used so far in preparing dinitrogen complexes fall into four major categories.

- a) The reaction of a metal complex with dinitrogen in the presence of other ligands, such as phosphines, and also, in most cases, in the presence of a reducing agent.
- b) The reaction of a metal complex with a nitrogen-containing reagent which gives rise to dinitrogen either as an oxidation product (e.g. N_2H_4 , N_3^-) or reduction product (e.g. N_2O).
- c) The coupling of a nitrogen-containing species to another nitrogen-containing species which is already attached to the metal through the nitrogen. The coupling produces dinitrogen which remains bound to the metal atom.
- d) The reaction of a dinitrogen complex with reagents to give a new complex in which the dinitrogen is retained.

Perhaps the most exciting preparative routes are those of the first group where the source of dinitrogen is gaseous dinitrogen or in some cases dinitrogen in the air. $FeH_2N_2(PPh_3)_3$,^{38,39} which has been investigated in the present work, has been prepared according to this method. Also some Ru,⁴⁰⁻⁴³ Os⁴³ and Co^{15,44,45} dinitrogen complexes have been prepared by this method.

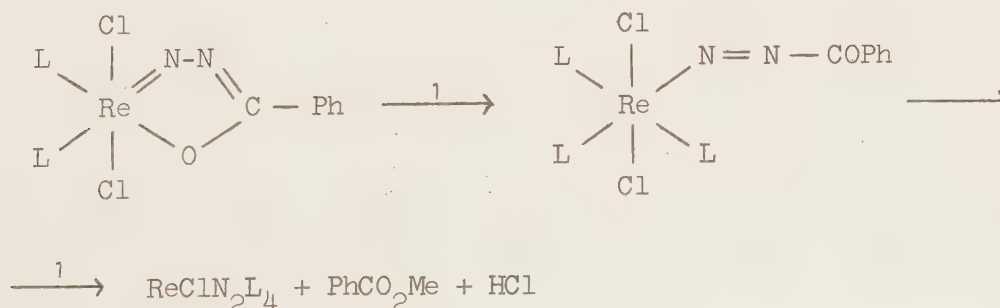
The formation of dinitrogen complexes using hydrazine and azides as the source of dinitrogen probably involves the coordination of

these molecules to the metal ion and subsequent oxidation to dinitrogen which remains coordinated to the metal. This method is the most frequently used in preparation of dinitrogen complexes of the type investigated in the present work. The complexes $\text{Os}(\text{NH}_3)_5\text{N}_2\text{X}_2$ have been prepared from K_2OsCl_6 and $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$.^{13,14,46} $\text{Ru}(\text{NH}_3)_5\text{N}_2\text{X}_2$ complexes were also prepared by the hydrazine method,¹ but it was later found that pure complexes were best prepared from $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ and NaN_3 .⁴⁷ Also the iridium complex $\text{IrClN}_2(\text{PPh}_3)_2$ ^{16,28,48} can be prepared according to this method, viz.



1 = CHCl_3 containing ethanol; L = PPh_3

In this reaction the oxidation state of the iridium does not change, but an oxidation state change does occur in the formation of the rhenium dinitrogen complexes, ReClN_2L_4 .¹⁷



1 = L + MeOH; (L = variety of phosphines)

A few examples of method (c) are the diazotization of ammonia⁴⁹ or azide⁵⁰ with nitrous acid where the dinitrogen produced on the

metal remains coordinated. These reactions lead to the formation of bisdinitrogen complexes, e.g. $\text{Os}(\text{NH}_3)_4(\text{N}_2)_2^{2+}$.⁴⁹

In a relatively few cases dinitrogen complexes can be converted to others, but generally this is not a good method as the dinitrogen is often readily displaced by other reagents even under mild conditions. A dinitrogen complex investigated in the present work, viz. $\text{IrClN}_2(\text{C}_8\text{H}_{12}\text{O}_4)(\text{PPh}_3)_2$, has been prepared according to this method through the reaction of $\text{IrClN}_2(\text{PPh}_3)_2$ with diethylmaleate in chloroform solution.^{28,48}

2.3 Stability of dinitrogen complexes in air and in solution.

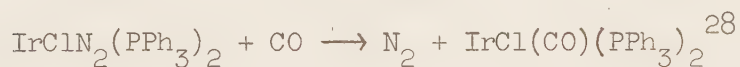
Stability in this connection means the kinetic stability. Most of the dinitrogen complexes are not stable in air for a long time, but must be kept in an inert atmosphere. The dinitrogen complexes of rhenium in the solid state are the most stable in air, but in solution they are slowly oxidized. The complexes $\text{Ru}(\text{NH}_3)_5\text{N}_2\text{X}_2$ and $\text{Os}(\text{NH}_3)_5\text{N}_2\text{X}_2$, $\text{X} = \text{Cl}^-$, Br^- , I^- , are also relatively stable in air and can be prepared and handled without decomposition. Aqueous solutions of $\text{Ru}(\text{NH}_3)_5\text{N}_2^{2+}$ and of $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$ are, however, not stable for a long time. The stability of these complexes also depends on the purity of the complex. The Ru complexes mentioned above readily blacken in air, especially in aqueous solution, if they are contaminated with hydrazine impurities. It has also been found that the Ru and Os dinitrogen complexes are light sensitive. The most instable dinitrogen complexes investigated in the present work are $\text{IrClN}_2(\text{PPh}_3)_2$ and $\text{FeH}_2\text{N}_2(\text{PPh}_3)_3$. They are not stable in air for more than a few minutes and in solution they are rapidly oxidized. These facts make it difficult to handle these two complexes

and all operations must be done rapidly.

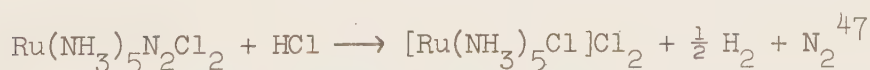
The majority of the dinitrogen complexes are stable only at room temperature and below. When heated they give off dinitrogen gas quantitatively. In the present work, the only complex with which there have been difficulties in this respect is $\text{FeH}_2\text{N}_2(\text{PPh}_3)_3$. The ESCA measurements have therefore been performed at low temperature, as the complex decomposes under vacuum at room temperature (paper VI).

2.4 Some chemical reactions of dinitrogen complexes.

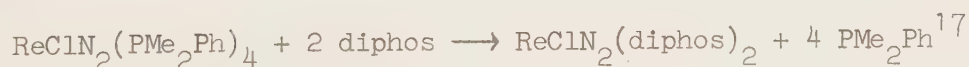
The most common reaction carried out on dinitrogen complexes is one where the dinitrogen is displaced. The ease with which this reaction proceeds makes the dinitrogen complexes useful starting materials for the preparation of other metal complexes. Only a few examples of general interest are given.



A reaction which has been utilized in the preparation of the starting complex for preparation of a pure Ru-N_2 complex is the following:



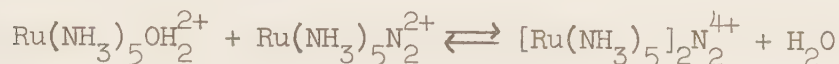
There are also some reactions which occur without loss of dinitrogen, e.g.



This reaction illustrates how strongly dinitrogen is bound to rhenium.

Many other reactions have been studied, especially for the ruthenium dinitrogen complexes.

The binuclear ion $[\text{Ru}(\text{NH}_3)_5]_2\text{N}_2^{4+}$ is thought⁴¹ to exist in equilibrium with a mononuclear dinitrogen complex in solution, viz.



This reaction has also been studied by kinetic measurements.³⁷

The formation of dimers with bridging dinitrogen suggests a coordination ability associated with coordinated dinitrogen. Also the reaction



has been studied by kinetic measurements.³⁷ The rate constants of these two last mentioned reactions have been found to be about the same,³⁷ suggesting that coordinated dinitrogen is about as reactive as dissolved dinitrogen, taking into account the solubility of dinitrogen in water. Further reports^{51,52} dealing with equilibria and rates of formation of the above mentioned complexes of ruthenium have recently appeared.

Interaction between coordinated dinitrogen and other metal ions has also been observed though definite compounds have not been isolated. It has been found³⁶ that the metal ions Ag(I) and Cu(II) do not release dinitrogen from the complex $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$ but the resulting products show large shifts of the N-N stretching vibration. It was suggested³⁶ that the coordinated dinitrogen acts as a donor, i.e. $(\text{NH}_3)_5\text{Os}-\text{N}\equiv\text{N} \longrightarrow \text{M}$, where M is Ag(I) and Cu(II). These results have, however, been questioned by Chatt et al.⁵³, who

propose that the observed bands at higher frequencies are assigned to oxidation products, e.g. $\text{Os}(\text{NH}_3)_5\text{N}_2^{3+}$ and $\text{Os}(\text{NH}_3)_5\text{N}_2^{4+}$, rather than to bridged complexes.

2.5 Electronic spectra.

Measurements of the electronic spectra of the dinitrogen complexes have largely been ignored, except for the investigation of the ultraviolet spectra of the ruthenium and osmium ammine dinitrogen complexes. The reported values of wavelength and molar absorption coefficients (ϵ) are given in Table 1.

Table 1

Complex ion	Wavelength nm	$\epsilon \times 10^{-4}$ $\text{M}^{-1} \text{ cm}^{-1}$	Reference
$\text{Ru}(\text{NH}_3)_5\text{N}_2^{2+}$	221	1.60	40,41
$[\text{Ru}(\text{NH}_3)_5]_2\text{N}_2^{4+}$	262	4.70	41
$\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$	208	2.50	49
$\text{Os}(\text{NH}_3)_4(\text{N}_2)_2^{2+}$	221	2.00	49

These values have been used to confirm the purity of the prepared dinitrogen complexes of Ru and Os in the present work.

2.6 Infrared spectra.

As mentioned in the introduction, the N-N stretching frequency of coordinated dinitrogen occurs in the range $2\,200 - 1\,900 \text{ cm}^{-1}$. The exact position is dependent on the metal and the other ligands in the complex. Another vibration frequency in the range $550 - 400 \text{ cm}^{-1}$ has been assigned to the M-N₂ stretching vibration in the complexes $\text{Ru}(\text{NH}_3)_5\text{N}_2^{2+}$ ⁴⁷ and $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$.⁴⁶ The assignment⁴⁷ is given on the

basis of comparison of spectra of the ruthenium dinitrogen complexes with spectra of ruthenium ammine complexes. Borod'ko *et al.*⁴⁶ based their assignment on deuteriation shifts. It has, however, been suggested²⁶ that this frequency can be the bending vibration (δ_{M-N_2}). Recently, a new assignment of the $M-N_2$ stretching vibration has been proposed⁵⁴ for $Ru(NH_3)_5N_2X_2$ based on deuteriation shifts and solid state Raman intensities. Earlier,⁴⁷ the highest frequency band in the metal-nitrogen stretching region ($550 - 400\text{ cm}^{-1}$) of the IR-spectra of $Ru(NH_3)_5N_2X_2$ has been assigned as largely ν_{Ru-N_2} , while the lower frequency bands have been assigned to ν_{Ru-NH_3} stretching motions. The far-infrared spectra of a $Ru-N_2$ complex and an $Os-N_2$ complex in the solid state are given in Fig. 1. It has now been

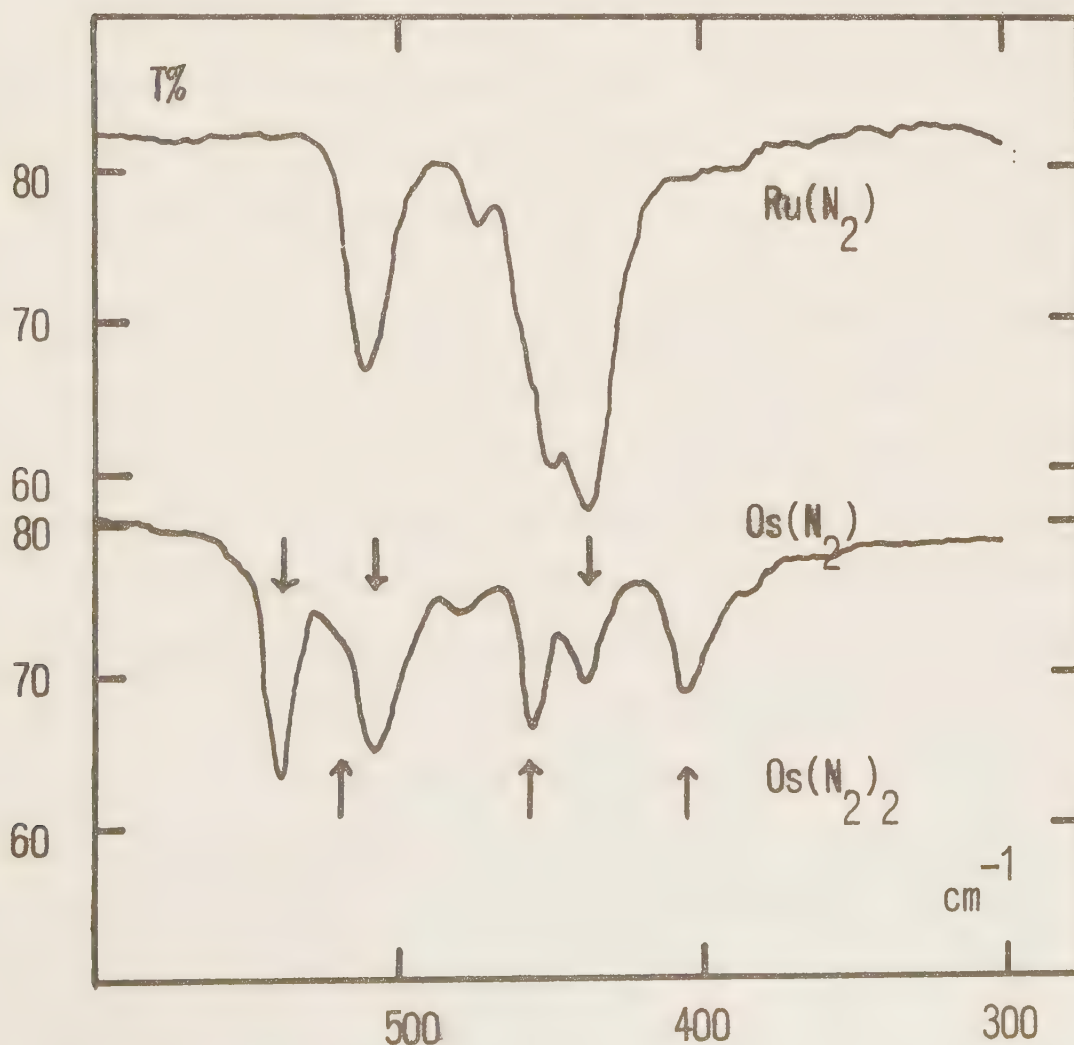


Fig.1.

proposed⁵⁴ that the lowest frequency band is the Ru-N₂ stretching vibration. In the present work the first proposed assignments^{46,47} are followed and intensities are measured on these bands. As can be seen in Fig. 1 the intensities of the highest and the lowest frequency band for the Ru-N₂ complex do not deviate much from each other and, consequently, charges of the same order of magnitude should result from any of the bands.

It has earlier been suggested²⁸ that the N-N stretching frequency is a good measure of the stability of dinitrogen complexes. It is now evident that this is not always the case. Where comparisons are possible, e.g. for Ru and Os ammine dinitrogen complexes, the strongest perturbation of the dinitrogen group is found for complexes formed by the third row transition metals and thus probably also the strongest M-N₂ bond is formed by the metals of the third row. Chemical evidence agrees with this.

Changes in the other ligands in the dinitrogen complexes have an effect on the N-N stretching frequency. Thus, in a series of similar complexes it appears that ν_{NN} decreases in the order $\text{PPh}_3 > \text{PPh}_2\text{R} > \text{PPhR}_2 > \text{PR}_3$. This would be expected because the more aliphatic phosphines are the more basic, and so they should consequently increase the electron density at the metal and cause greater electron drift into the antibonding orbitals of the dinitrogen ligand. Nevertheless, despite the greater back donation, the dinitrogen complexes containing the more aliphatic phosphines are the less stable. The trend in ν_{NN} mentioned above has been found within series of dinitrogen complexes of Co,⁵⁵ Os⁵⁶ and Ir.²⁹

The ionic ammine complexes of $\text{Ru}^{1,47}$ and Os^{14} show marked counter ion effects on the frequency ν_{NN} . It has thus been found that the frequency ν_{NN} increases while $\nu_{\text{M-N}_2}$ decreases in a series of complexes with counter ions, viz. Cl^- , Br^- , I^- , ClO_4^- , BF_4^- and PF_6^- . The trend can be explained in terms of polarization of the dinitrogen ligand by the anion. The smaller the anion the greater the polarization, which corresponds to a lower N-N stretching frequency and a higher M-N₂ stretching frequency. Recently, however, Chatt et al.⁵⁷ have proposed, on the other hand, that the interaction of anions is a polarisation of the hydrogen of the ammine ligands which leads to a greater electron release to the metal and thence into the π -antibonding orbitals of the N-N bond. The smaller the anion radius the greater the electron release and the lower the ν_{NN} . Counter ion effects are also observed in the present investigation and will be further discussed later.

Some structural information can be obtained from the infrared spectra of certain dinitrogen complexes. For example, the absence of an infrared band (ν_{NN}) for the binuclear ion, $[\text{Ru}(\text{NH}_3)_5\text{N}_2]^{4+}$,⁴¹ indicates a symmetrical dinitrogen bridge. Its presence in the Raman spectrum confirms this.⁵⁸ The bisdinitrogen complexes of Os^{49} show two N-N stretching vibration bands, which suggests a cis-configuration. Some bisdinitrogen complexes of molybdenum³⁴ and tungsten³⁵ show only one N-N band, suggesting a trans-configuration.

2.7 Bonding.

A number of facts must be taken into account when the bonding between dinitrogen and a metal ion is described.

a) The metal -N-N bond system is linear.

- b) The N-N stretching frequency is reduced about 100 to 400 cm^{-1} from that of free dinitrogen on coordination.
- c) The coordination of strong π -acceptor ligands to a metal ion already coordinated to dinitrogen causes an increase in the N-N stretching frequency, and presumably a reduction in the M-N_2 bond strength occurs.
- d) The N-N stretching frequencies for bisdinitrogen complexes are quite high and the complexes are generally less stable than related monodinitrogen complexes.
- e) The metal ions that most readily form dinitrogen complexes have the d^6 and d^8 spin paired configurations, systems which are good π -donors.

The bonding is represented diagrammatically in Fig. 2.

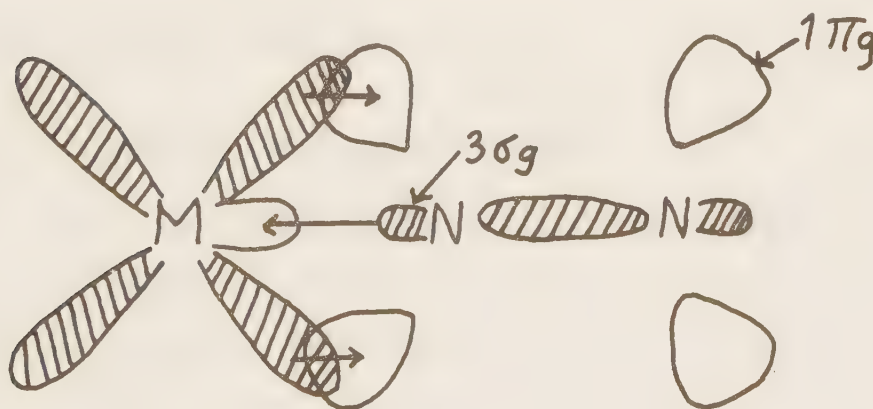


Fig. 2.

The highest filled $3\sigma_g$ orbital of nitrogen, behaving as a donor, forms a σ -bond with a vacant metal orbital of similar symmetry. Back donation of metal electrons from filled d orbitals into the antibonding $1\pi_g$ orbitals of dinitrogen results in a metal- N_2 π -bond. Therefore, the reduction in the N-N stretching frequency on

coordination corresponds to a reduction in the N-N bond order.

The evidence that π -bonding is important comes from c) and e) above, i.e. changes in the π -acceptor properties of the other ligands alter the π -bonding to dinitrogen (as seen by a change in ν_{NN}), and dinitrogen complexes are mainly formed with metals capable of acting as π -donors. Further, when two dinitrogens are bound to the same metal they will compete for the π -electrons and thus give rise to an overall reduction in the M-N₂ bond strength, as observed by a significant rise in the N-N stretching frequency for such complexes.

3. EXPERIMENTAL PROCEDURES

3.1 Infrared spectral measurements.

All spectra on the N-N and M-N₂ stretching vibrations were recorded on an expanded abscissa scale. Proper attention to optimum settings of the instrument variables was emphasized. When the N-N absorption bands were of low intensity, which was the case for the extracted dinitrogen complexes of Ru and Os (paper II) and for the spectra on aqueous solutions of Os (paper III), ordinate expansion was used as well. Measurements on the dinitrogen complexes have been performed both in the solid state and in solution. It is desirable to use as many solvents as possible to investigate specific effects and medium effects. The complexes are, however, not soluble in so many solvents. The chloride and bromide salts of Ru and Os were

soluble only in water and in very low concentrations. The iodide salts of the same metals were soluble only in DMSO and DMF in measurable concentrations. The dinitrogen phosphino complexes of Ir and Re were soluble in chloroform and benzene. It is thus difficult to make comparisons between all the investigated complexes as they are measured in different solvents. All the complexes have, however, been examined in the solid state (as KBr disks).

Calibrated 0.2 mm cells with CaF_2 -windows were used in all measurements, except for aqueous solutions where 25 μ spacers were used.

For each dinitrogen complex, measurements were performed on at least two preparations and at a number of concentrations. Linear Beer's law plots were observed for all the complexes in all solvents. All measurements on the complexes in solution were performed immediately after complete dissolution, since it was found that the complexes decompose more or less rapidly in solution.

The absorption intensity, defined as $\frac{2.303}{c \cdot l} \int_{\text{band}} \log I_0/I \, d\nu$, where c is the concentration in M and l is the cell path length in cm, has been obtained through graphical integration of the curves $\log I_0/I$. $\epsilon = \frac{\log I_0/I}{c \cdot l} = \epsilon(\nu)$, which were calculated from the transmission bands recorded by the instrument. Later, when the instrument was equipped with a linear absorbance potentiometer, absorption band areas were determined with a planimeter. All reported intensity values are mean values of intensities determined at different concentrations. The maximum deviation from the mean value is generally about 10 %. The largest deviation is found in the values measured in KBr as dispersion medium.

The weak band assigned to the $M-N_2$ stretching vibration in the Ru and Os ammine dinitrogen complexes is observed only in spectra measured in KBr. In solution the concentration of the complex is too small to get any measurable band. $M-N_2$ intensities in solution have therefore been estimated as described in paper I. The far-infrared spectra of the dinitrogen complexes containing phosphine ligands are complicated by the fact that the phosphine ligands show strong absorption in the range $600 - 400\text{ cm}^{-1}$. This makes it impossible to observe the weak band corresponding to the $M-N_2$ stretching vibration in these complexes.

3.2 Short introduction to the ESCA method.

Photoelectron spectroscopy is a recent addition to the arsenal of spectroscopic tools now available to chemists. It makes possible a direct observation of molecular orbital energy levels as well as inner electron or core electron levels. In photoelectron spectroscopy, the electrons are expelled from the sample by means of photons and their energy is analyzed in a high-resolution spectrometer.

UV excitation expels electrons from the valence region. This branch of photoelectron spectroscopy was pioneered in the early sixties by Turner⁵⁹ who recognized its importance for the investigation of molecular orbitals. The core electrons are accessible only by X-ray excitation. The core electron orbitals of atoms in molecules are essentially atomic in character and have traditionally been regarded as chemically inert. They were therefore almost forgotten by chemists until the advent of ESCA, which demonstrated their usefulness in chemistry. ESCA originated with the development of high resolution electron spectrometers by Siegbahn. A few years later, chemical shifts⁶² between core electron lines were also

discovered (1957). Siegbahn and coworkers realized the significance of this for chemical applications and therefore coined the now wellknown acronym ESCA (Electron Spectroscopy for Chemical Analysis). Although ESCA is not restricted to core electrons it is often used as a synonym for core photoelectron spectroscopy. There are now some monographs^{24,59,61} available dealing with aspects of photoelectron spectroscopy.

3.3 Chemical shifts and correlation with charge.

When an atom is bound chemically to other atoms there is a change of the wave function for the valence electrons. Consequently, there is a change in the interaction between the valence electrons and the core electrons and this induces a slight change in the binding energies of the core (and valence) electrons. Therefore, a change in chemical environment of an atom is relayed to its core electrons and can be observed as a line shift in the ESCA spectrum. These chemical shifts of the inner electron energies can be measured and are likely to assist in the solution of many problems in chemistry. A particular feature of ESCA is that one obtains information on chemical bonding and molecular structure by measuring a quantity that remains essentially atomic in character. Thus, one can move the area of inspection from one atomic species to the other in the molecular structure. In the application of ESCA to chemical problems, it is desirable to be able to explain the chemical shifts by means of a simplified chemical language. Correlations between chemical shifts and an atomic charge parameter have been empirically established.

In an early study of inorganic sulphur compounds the chemical shifts were correlated with the formal oxidation state.⁶² Atomic charges, estimated by means of Pauling's concept of partial ionic character, have been correlated with measured binding energies in sulphur,²⁴ nitrogen⁶³ and carbon⁶⁴ compounds. Also, more elaborate theoretical calculations, e.g. extended Hückel and CNDO calculations of the charge distribution in nitrogen compounds,⁶⁵ have been performed and correlated with ESCA data. In the present work N1s binding energies have been redetermined for some of the nitrogen compounds measured by Hendrickson et al.⁶⁵ These binding energies have been plotted against charge calculated by Hendrickson et al.⁶⁵ The correlation diagrams thus obtained have been used in the estimation of the charge on the nitrogen atoms in the dinitrogen complexes. Nitrogen atom charges from ab initio SCF MO calculations have been determined⁶⁶ as well and correlated with N1s binding energies measured in the present work. The correlation between N1s binding energy and calculated charge seems to be linear in all diagrams (Figs. 3-5 in paper V).

3.4 Excitation and recording of photoelectron spectra.

When electrons are expelled from a sample by means of photons they acquire a kinetic energy, E_{kin} , which is equal to the difference between the photon energy, $h\nu$, and the electron binding energy, E_b , viz.

$$E_b = h\nu - E_{\text{kin}} - \phi_{\text{spec}}$$

ϕ_{spec} is a constant including the work function of the spectrometer. E_{kin} is measured with high accuracy and the quantity $h\nu$ is well defined by the choice of a monochromatic source of excitation. The

measurements have been performed under a vacuum of 10^{-7} torr and all spectra were obtained with AlK_{α} -radiation (1486.6 eV). The instrumental resolution was such that the half-width of the gold $4f_{7/2}$ electron peak was 1.30 eV under the experimental conditions in this work.

As ESCA is a surface method^{24,67} it is of importance how the surface is constituted during the measurements. In the solid state, the photoelectrons originate from the surface of the sample and have an escape depth of 20 - 100 Å.^{24,68} Electron spectroscopy can thus be used for investigation of specific problems in surface chemistry. The surface sensitivity of ESCA requires clean surfaces of the samples when investigating bulk properties.

In the present work the following sample preparation technique was used. The compounds were dissolved in a suitable solvent and one or two drops of the solution or suspension were immediately placed on a well cleaned platinum foil. A thin film of the compound was obtained on the foil after evaporation of the solvent. If the film was not too thick, it was possible to register platinum signals and thus refer measured binding energies to a fixed platinum peak. As reference peak, that of Pt $4f_{7/2}$ electrons has been chosen, which was found to have $E_b = 71.1$ eV, a value in good agreement with the literature.⁶⁹ All reported binding energy values are consequently referred to the binding energy of Pt $4f_{7/2}$ electrons. The reproducibility of the photoelectron peaks was within 0.1 eV. Another advantage with the preparation procedure used here was that no charging effects were observed during the measurements, i.e. the peaks have the same positions in spectra recorded several times

after each other. Charging effects depending on sample thickness have recently been investigated by Johansson et al.⁷⁰ Their results are in agreement with our findings.

4. THE RESULTS OF THE INFRARED SPECTROSCOPIC MEASUREMENTS

4.1 Infrared absorption intensities of the N-N stretching vibration in the dinitrogen complexes.

In paper I the results of the intensity measurements on the dinitrogen complexes of Ru and Os are presented. In this work it was found that the osmium dinitrogen complexes had a higher intensity of the N-N stretching vibration than the ruthenium dinitrogen complexes. The N-N stretching frequency (ν_{NN}) was lower in the osmium than in the ruthenium dinitrogen complexes and therefore a rough generalization was made, viz. the higher the frequency (ν_{NN}) the lower the absorption intensity (A_{NN}). This A_{NN} versus ν_{NN} plot showed a large scattering, which may indicate that several factors influence this relation, e.g. counter-ion effects and solvent effects. These effects will be described below. To further investigate the correlation between intensity (A_{NN}) and frequency (ν_{NN}), the measurements have been extended to dinitrogen complexes of iridium and rhenium (paper IV). It is evident that the correlation also holds for these complexes, and the correlation now covers a frequency range 2 200 - 1 900 cm^{-1} . In Fig. 3 all measured intensity values (A_{NN}) for the dinitrogen complexes are plotted against frequency (ν_{NN}). The unusually high values at 2 007 cm^{-1} and 2 020 cm^{-1} are

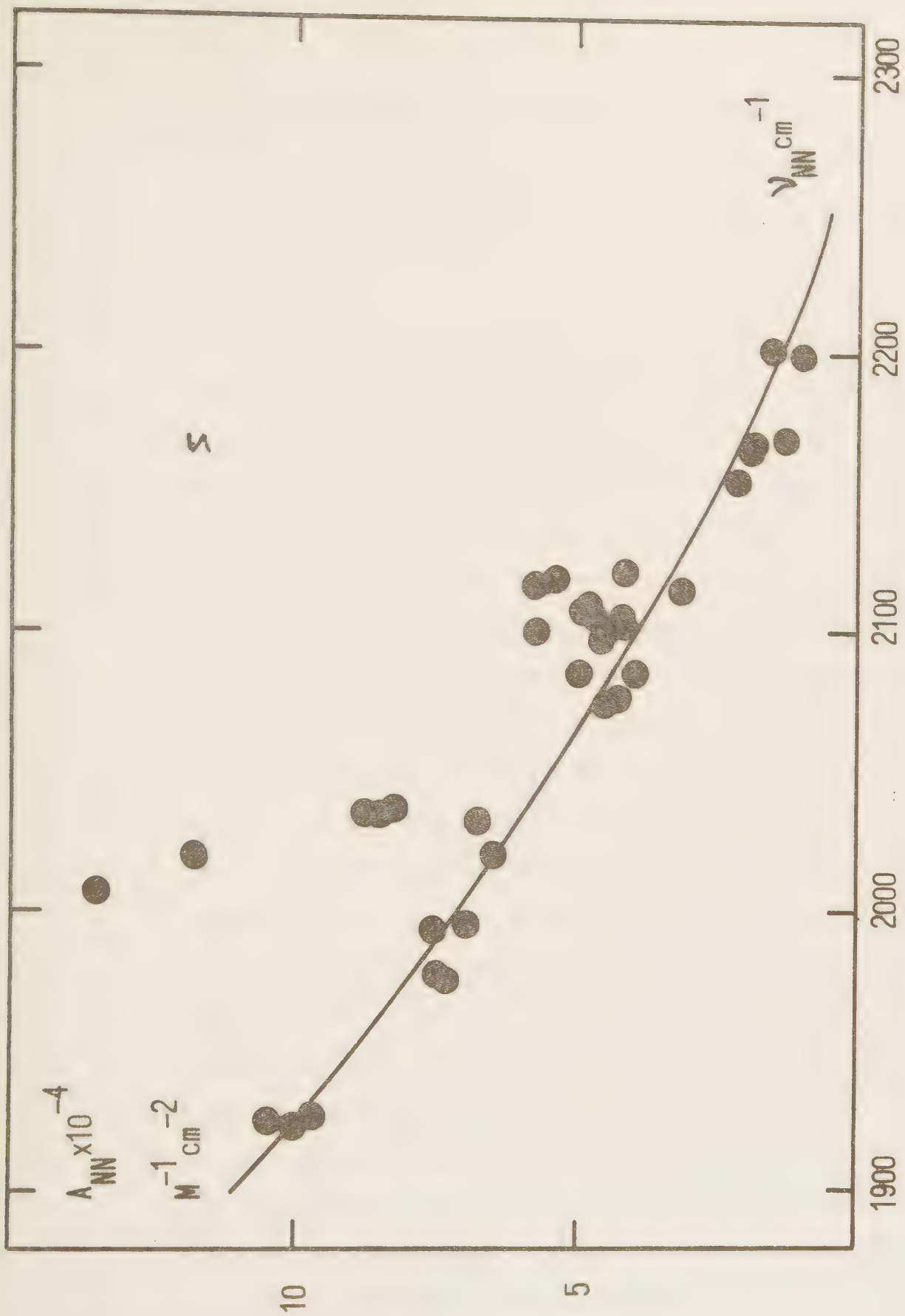


Fig.3.

those of $\text{Os}(\text{NH}_3)_5\text{N}_2\text{I}_2$, which will be discussed below. It is evident from Fig. 3 that the intensity (A_{NN}) approaches zero, when the frequency (ν_{NN}) approaches the limiting value for the free dinitrogen molecule, i.e. $2\,331\text{ cm}^{-1}$.¹⁸

Qualitatively, the observed intensities of the N-N stretching vibration can be discussed in terms of the degree of $d\pi-p\pi^*$ back donation from the metal ion to the dinitrogen ligand and the degree of σ -bonding from the lone-pair of the dinitrogen ligand to the metal ion. A high electron density in the antibonding π -orbitals of the dinitrogen group corresponds to an increase in the N-N distance. Conversely, when the N-N distance increases during the vibration there will be a flow of electrons into these antibonding π -orbitals. The N-N stretching vibration is thus followed by a change of the electron density over the M-N-N entity. This corresponds to a large variation of the dipole moment during the vibration, which means a high infrared absorption intensity. As the rhenium dinitrogen complexes have the highest intensities of the N-N stretching vibration, it is reasonable that the degree of $d\pi-p\pi^*$ back donation is greatest in these complexes. It then follows that an effect that causes a weakening of the N-N bond strengthens the M-N_2 bond to a corresponding extent. Thus, when the degree of $d\pi-p\pi^*$ back donation is high, the disturbance of the dinitrogen ligand must be considerable and there will be a decrease in the N-N bond order. A high intensity value of the N-N stretching vibration thus gives an indication of a strong metal-dinitrogen bond. In agreement with this, it has been found that the most stable dinitrogen complexes both in the solid state and in solution are those of rhenium. The dinitrogen complexes of iridium and iron are considerably more instable. These complexes

also show lower values of the intensity (A_{NN}) than the rhenium complexes.

4.2 Solvent effects on intensity (A_{NN}) and frequency (ν_{NN}) in the dinitrogen complexes.

The good agreement on the measured intensity values (A_{NN}) for different dispersion media, which has been found for the dinitrogen complexes of rhenium, iridium and iron, indicates that the intensity apparently is not dependent on the medium.

For the dinitrogen complexes of ruthenium and osmium the situation is different. It has thus been found that the intensity values measured in the solid state always are lower than the values determined in solution. The frequency (ν_{NN}) is also changed in different solvents. For aqueous solutions, ν_{NN} is larger than for the solid state, whereas ν_{NN} in DMSO and DMF has a lower value than in the solid state. The fact that the chloride and bromide salts of osmium have equal values of both intensity (A_{NN}) and frequency (ν_{NN}) in aqueous solution indicates that these salts are completely dissociated in water. Especially the equal values of the frequency are an indication of no influence of the counter-ions. The same is also valid for the corresponding ruthenium salts.

An obvious solvent effect is found for $\text{Os}(\text{NH}_3)_5\text{N}_2\text{I}_2$ dissolved in DMSO and DMF. A large increase in intensity (A_{NN}) which was paralleled by a decrease in ν_{NN} was found. This effect has been explained as a charge-transfer association of outer-sphere ligands (paper I). Such an effect was not so noticeable for the corresponding ruthenium compound, probably because the ion-radius of

ruthenium is somewhat smaller than for osmium and thereby the possibility of near contact between the solvating molecules and the d-orbitals engaged in an electron-donation process must be smaller for ruthenium than for osmium. The bisdinitrogen complex, $\text{Os}(\text{NH}_3)_4(\text{N}_2)_2\text{I}_2$ dissolved in DMSO does not show any large intensity value (A_{NN}). It can then be assumed that the degree of association of the >S=O groups to the metal ion must also depend on the charge on the metal ion. As there is a greater influence from the solvent for the monodinitrogen complex, it is reasonable that there is a smaller charge on the metal ion in the bisdinitrogen complex. This suggestion has been checked with the ESCA method (paper V), which shows that the positive charge on the metal ion can be somewhat smaller in the bisdinitrogen complex than in the monodinitrogen complex.

It can, however, not be excluded that it could be the association of iodide ions to the osmium complex in DMSO and DMF rather than the solvent molecules that causes the great intensity of the N-N stretching vibration.

4.3 Counter-ion effects on intensity (A_{NN}) and frequency (ν_{NN}) in the dinitrogen complexes of Ru and Os.

It has been mentioned above that the dinitrogen complexes $\text{Ru}(\text{NH}_3)_5\text{N}_2\text{X}_2$ and $\text{Os}(\text{NH}_3)_5\text{N}_2\text{X}_2$ show marked counter-ion effects. The frequency ν_{NN} increases in a series of complexes with counter-ions, $\text{Cl}^- < \text{Br}^- < \text{I}^-$. The intensity (A_{NN}) has been measured in the solid state and for $\text{Ru}(\text{NH}_3)_5\text{N}_2\text{X}_2$ this has been found to decrease in the order $\text{Cl}^- > \text{Br}^- > \text{I}^-$. For $\text{Os}(\text{NH}_3)_5\text{N}_2\text{X}_2$, on the other hand, the intensity value for the iodide is greater than the corresponding chloride

and bromide values. It is plausible that an outer-sphere effect is responsible for the high value of the osmium iodide. It is, however, disturbing that the frequency increases with increasing intensity. A similar effect is found if one regards the intensities of the $M-N_2$ stretching vibration in the solid state. It has been found that both the frequency ν_{M-N_2} and the intensity A_{M-N_2} decrease in the order $Cl^- > Br^- > I^-$. On comparison of the frequencies ν_{NN} and ν_{M-N_2} , it is found that while ν_{M-N_2} decreases in the order $Cl^- > Br^- > I^-$, ν_{NN} increases in the order $Cl^- < Br^- < I^-$.

The observed effects for the Ru and Os dinitrogen complexes are specific for these complexes, since such effects have not been observed for other complexes. Chatt et al.⁵³ have found that the N-N stretching frequency in salts of $[ReClN_2[Ph_2P(CH_2)_2PPh_2]_2]^+$ is independent of the nature of the anion.

To get further information about the influence of counter-ions on frequency and intensity of the N-N stretching vibration, some sulphur containing anions have been complexed with the dinitrogen complexes of Ru and Os (paper II). These complexes have been extracted into water-saturated butanol and pentanol and the intensity of the N-N stretching vibration has been measured. It was found that the intensities (A_{NN}) were lower than those measured on the halide complexes (paper I). This was found for both the ruthenium and osmium complexes. The frequency (ν_{NN}) in the extracted complexes has changed very little compared with the frequency (ν_{NN}) in the halide complexes. The frequencies (ν_{NN}) are also almost the same, independent of anion within the ruthenium and osmium complexes, despite the variation in intensity. It was also observed that the intensity became lower as the size of the anion increased. It has been suggested

that the explanation of these results is the polarizability of the anions. Thus, it is quite probable that it is the change in the dipole moment of the whole extracted complex, e.g. $M(NH_3)_5N_2(dtc)_2$, during the normal vibration which determines the intensity for the observed band. As the M-N-N group gives rise to strong infrared absorption, charges will move to and fro over the group during the vibration. These charges induce a dipole moment in the easily polarizable outer-sphere, which is of opposite direction to that of the M-N-N group. Thus, the total dipole moment will be smaller which causes a lower intensity of the N-N stretching vibration. The fact that the intensity A_{NN} decreases with increasing size of the anion supports the view that it is the polarizability of the anion that influences the dipole moment change of the entire extracted unit. It is, however, remarkable that the frequency (ν_{NN}) does not change when the intensity (A_{NN}) is changed. This means that the electronic structure within the M-N-N unit is not changed and that the force constant of the N-N band is practically constant.

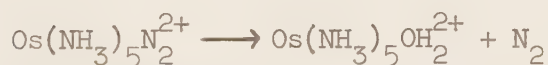
In this investigation (paper II) a remarkable solvent effect on the intensity (A_{NN}) was found. The intensities measured in butanol were always about 20 % higher than those in pentanol. It has been suggested that it could be the water content in the alcohols, that causes the intensity of the N-N stretching vibration band to differ in the two solvents.

4.4 Decomposition of $Os(NH_3)_5N_2^{2+}$ in aqueous solutions (paper III).

This investigation was started since one of the major problems in preparing $Os(NH_3)_5N_2Cl_2$ was that the product also contained a considerable amount of a bisdinitrogen complex, viz. $Os(NH_3)_4(N_2)_2Cl_2$,

which was observed in the infrared spectrum. The frequencies (ν_{NN}) are different in the two complexes, indicating different perturbations of the dinitrogen groups, and therefore it can be expected that the complexes will have different stabilities in solution. Indeed, such a difference in stability is easily observed.

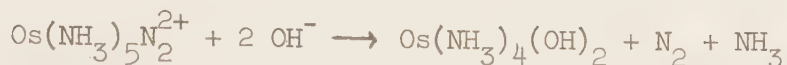
The decomposition of $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$ in aqueous solutions at different pH and temperatures has been studied by measuring the absorbance of the N-N band at $2\,035\text{ cm}^{-1}$. It has been found that the decomposition in both acid and alkaline solutions is more complicated than what corresponds to a pure first order reaction. It has thus been found that the $\log(\log T_0/T)$ versus time straight lines bend downwards at a certain value of the time, indicating that the decomposition reaction becomes more rapid than for the first order reaction. Such behaviour is expected for an autocatalytic reaction. In acid solution it is a homogeneous catalysis, while in alkaline solution there probably is a heterogeneous catalysis. The first main step of the decomposition in acid solution can be described as



When the decomposition is catalyzed by the product a binuclear complex probably forms, which then readily decomposes and dinitrogen is lost.

In the alkaline solutions, the decomposition rate of $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$ was found to increase when a precipitate had been formed in the solutions. The decomposition in alkaline solution was found to be more complicated than in acid solution. A new band at $1\,993\text{ cm}^{-1}$ besides the main band at $2\,035\text{ cm}^{-1}$ indicates that a new species is formed. The decrease in absorbance of the N-N band at $2\,035\text{ cm}^{-1}$

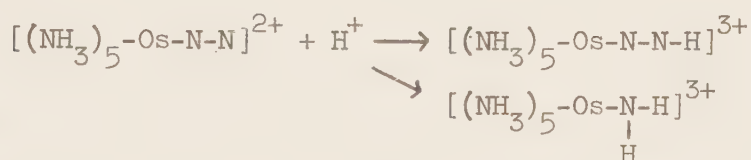
indicates that dinitrogen is lost. The situation is discussed in detail in paper III. The mechanism of the decomposition in alkaline solution has been described as



The solid, $\text{Os}(\text{NH}_3)_4(\text{OH})_2$, then loses ammonia and the final product is probably $\text{Os}(\text{OH})_2$. The mechanism of the autocatalysis is difficult to elucidate, but as the decomposition became more rapid when a precipitate was formed in the solution it probably is a heterogeneous catalysis.

When investigating the decomposition of $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$, the two N-N bands in the infrared spectrum which are assigned to $\text{Os}(\text{NH}_3)_4(\text{N}_2)_2^{2+}$ do not decrease in absorbance during the measurements. This has been found both in acid and in alkaline solutions. The decomposition of $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$ in acid solution has been followed until the band at 2035 cm^{-1} has disappeared and then the bisdinitrogen complex has been precipitated and identified through IR- and UV-spectra. Thus, the bisdinitrogen complex has been separated from the monodinitrogen complex through its greater stability in solution. This is remarkable since the bisdinitrogen complex is expected to be more instable than the monodinitrogen complex, since the frequency of the N-N stretching vibration is higher for the bisdinitrogen complex than for the monodinitrogen complex (cf. the discussion in Ref. 28). It was a great advantage when the bisdinitrogen complex could be separated from the monodinitrogen complex in this way, since now intensities (A_{NN}) could be determined more accurately than before when they were determined from a mixture of the two complexes.

To get a reasonable explanation of the stability of the bisdinitrogen complex in solution, the charges on the nitrogen atoms must be considered. It has been found by ESCA measurements on iridium and rhenium dinitrogen complexes (paper V) that both the nitrogen atoms are negatively charged. The lower the N-N stretching frequency, the greater is the negative charge on the nitrogen atoms. It is quite reasonable that a first step in the decomposition in acid solution is



and that these tervalent complexes then decompose. As the N-N stretching frequency is higher in the bisdinitrogen complex than in the monodinitrogen complex, the negative charges on the nitrogen atoms in the bisdinitrogen complex are smaller than the corresponding charges in the monodinitrogen complex. Thus, the bisdinitrogen complex probably shows smaller affinity to protons than the monodinitrogen complex and can be the most stable in acid solution.

The stability of the bisdinitrogen complex in alkaline solution can be explained by assuming that the hydroxide ions attack the central metal atom in the complexes. It has been found by ESCA that the charge on the metal ion is somewhat smaller in the bisdinitrogen complex than in the monodinitrogen complex. Thus, if there is a nucleophilic attack in alkaline solution, this is certainly more pronounced for the monodinitrogen complex than for the bisdinitrogen complex, which thus can be the most stable.

5. CHARGE DISTRIBUTION IN THE DINITROGEN COMPLEXES

5.1 Nitrogen 1s electron spectra of the dinitrogen complexes.

The nitrogen 1s electron spectra of the rhenium dinitrogen complexes show two well resolved peaks, indicating²⁴ different effective charges on the nitrogen atoms. It was also found that the N1s binding energy separation varied from one complex to another. The iridium complex, $\text{IrClN}_2(\text{PPh}_3)_2$, also gave two N1s electron peaks of low intensity and with a smaller difference in N1s binding energy than the corresponding rhenium dinitrogen complexes. The iron complex, $\text{FeH}_2\text{N}_2(\text{PPh}_3)_3$, described in paper VI, gave only one broad N1s electron peak, indicating a smaller polarity on the dinitrogen ligand in this complex. The charges on the nitrogen atoms have been estimated as described in paper V. It has been found that both the nitrogen atoms in the complexes are negatively charged. This fact indicates an increase of the electron density over the dinitrogen ligand caused by back donation from filled metal d-orbitals to antibonding π -orbitals of dinitrogen. This result thus confirms and strengthens the earlier results from the infrared intensity measurements. The total charge on the dinitrogen group was about 0.7 - 0.9 a.u. The greatest negative charge was found for the dinitrogen complex, which gave the highest intensity value (A_{NN}). A smaller negative charge on the dinitrogen ligand was obtained for complexes which show lower intensities (A_{NN}), e.g. $\text{IrClN}_2(\text{PPh}_3)_2$ and $\text{FeH}_2\text{N}_2(\text{PPh}_3)_3$.

Nitrogen 1s electron spectra of the ruthenium and osmium dinitrogen complexes show an almost symmetrical peak arising from the nitrogen in ammonia and the nitrogen in the dinitrogen ligand. The expected two N1s electron peaks from coordinated dinitrogen are overlapped by the peak from nitrogen in ammonia. It has not been possible to

resolve the N1s electron peaks into components and consequently no information about the charge distribution on the dinitrogen ligand in these complexes could be obtained.

5.2 Comparison of the separation in N1s binding energy with the N-N stretching frequency.

It is of interest to compare the magnitude of the separation in N1s binding energy with the N-N stretching frequency in the dinitrogen complexes. The largest difference in N1s binding energy (2.1 eV) was found for the complexes which show the lowest frequency (ν_{NN}). A much smaller difference was found for $\text{FeH}_2\text{N}_2(\text{PPh}_3)_3$, viz. 1.1 eV. The frequency (ν_{NN}) in this complex was $2\,075\text{ cm}^{-1}$.

When the difference in N1s binding energy is large the charge separation is large. Thus, for the complex $\text{ReClN}_2(\text{PMe}_2\text{Ph})_4$, the shift 2.1 eV corresponds to a charge separation of 0.25 a.u. (CNDO charges). The shift 1.1 eV corresponds to a charge separation of 0.13 a.u.

These observations can be rationalized in the following way: the larger the charge difference, the larger the repulsion between the nitrogen atoms and the lower the N-N stretching frequency. Combining this with earlier observations one can conclude that the stronger the dinitrogen ligand is bound to the metal, the more pronounced is the charge separation on the nitrogen atoms.

Another interesting observation is that the difference in N1s binding energy of the terminal nitrogen atom for the various dinitrogen complexes is not so pronounced (cf. Table 1, paper V) and

consequently, the charges on the terminal nitrogen atoms are more similar than the charges on the inner nitrogen atoms.

5.3 The fixed charge model applied to the dinitrogen complexes.

To get approximate information about the polarity of the $M-N_2$ bond in the Ru and Os dinitrogen complexes, the fixed charge model has been applied. The complex is considered as a two-atomic molecule consisting of $(NH_3)_5M$ and N_2 . For a two-atomic molecule, the absorption intensity is related to the dipole moment of the molecule by the formula (cf. e.g. Ref. 71)

$$A = \frac{\pi \cdot N}{3c^2 \times 10^3 \times \mu_{red}} \left(\frac{d\mu}{dr} \right)^2$$

Here N and c stand for the Avogadro number and the velocity of light. If it is assumed that the charges on the molecular fragments are $+q$ and $-q$ (atomic units), the dipole moment is

$$\mu = r \cdot q$$

If, as stated in the fixed charge model, it is assumed that q does not change with r , it follows that

$$\frac{d\mu}{dr} = q$$

In the calculation of $\frac{d\mu}{dr}$, intensities of the $M-N_2$ stretching vibration in aqueous solution were used, since counter-ion effects are assumed to be small in these solutions. The following values of q are obtained: for the Ru complexes $q = 0.72$ a.u. and for the Os complexes $q = 1.1$ a.u. These values are compared with a theoretical calculation for a hypothetical $Fe(O)-N_2$ complex, made by Kruglyak and Yatsimirskii.⁷² These authors found the following charge

distribution within the complex

$$\begin{array}{ccccc}
 \text{Fe} & - & \text{N} & - & \text{N} \\
 -0.432 & & +1.01 & & -0.576
 \end{array}$$

If the obtained values of q and $q_{\text{Fe}} = 0.43$ a.u. are plotted against the atomic number of the metal, a monotonous function is obtained.

It is thus evident that the charge separation increases in the order $\text{Fe} < \text{Ru} < \text{Os}$. As the calculated charge on the Fe atom is negative, it must be the σ -bond from the dinitrogen group to the metal atom that to the greatest extent determines the equilibrium charge distribution within the complex. The σ -bond thus increases in the order $\text{Fe} < \text{Ru} < \text{Os}$. This is to be compared with the suggestion that it is the $d\pi-p\pi^*$ back donation that to the greatest extent determines the change in frequency and intensity. It must, however, be pointed out that the fixed charge model is an oversimplification. It is quite reasonable that there is a variation of charge with interatomic distance. A term relating to this, viz. $\frac{dq}{dr}$, is easily derived from $\mu = rq$, i.e.

$$\frac{d\mu}{dr} = q + r \frac{dq}{dr}$$

To determine $\frac{dq}{dr}$, the charge q and the interatomic distance r must be known. $\frac{d\mu}{dr}$ is determined from infrared intensity data. The charge q on the nitrogen atoms in the dinitrogen complexes of Ru and Os could not be determined with ESCA and therefore $\frac{dq}{dr}$ could not be calculated for these complexes. The only information from the fixed charge model for the Ru and Os complexes is thus that the charge separation increases when the diminishing of the N-N bond order becomes more pronounced.

It must, however, be pointed out that the total charge on the dinitrogen group, calculated by the Russian workers,⁷² was positive, in contrast to the results from the ESCA measurements on dinitrogen complexes in the present work. One can therefore assume that these calculations are not correct.

The fixed charge model has also been applied to the dinitrogen complexes of rhenium and iridium. For these complexes the intensity of the $M-N_2$ stretching vibration is not known and calculations similar to those for the Ru and Os complexes could not be performed. Instead, the complexes of rhenium and iridium are considered as two-atomic molecules, viz. consisting of e.g. $(PhMe_2P)_4ClReN$ and N . From intensities $\{A_{NN}\}$ measured in chloroform solution, the quantity $\frac{d\mu}{dr}$ was calculated. The charges have been determined with ESCA (paper V), but the distance r is more difficult to obtain, since it is the distance between two charge centres and it is difficult to know where the charge centre on the big molecular fragment should be placed. It is thus impossible to obtain a true value of $\frac{dq}{dr}$. In paper IV, a calculation of $\frac{dq}{dr}$ using the limiting values of r , viz. $r_{N_1-N_2}$ and r_{M-N_2} for the complex $ReClN_2(PMe_2Ph)_4 (M-N_1-N_2)$, has been performed. It was further assumed that the terminal nitrogen atom carries the greatest negative charge. The following two values were obtained: $-\frac{dq}{dr} = 1.55$ a.u. and $-\frac{dq}{dr} = 0.54$ a.u. If it was assumed that the terminal nitrogen atom carries the smallest negative charge, the $-\frac{dq}{dr}$ -values became 1.67 a.u. and 0.58 a.u. The correct value of $-\frac{dq}{dr}$ probably lies closer to the smallest than the highest of the two calculated values above, as the correct value of the distance r is rather r_{M-N_2} than $r_{N_1-N_2}$. Calculations on the other dinitrogen complexes have not been

performed, since no interatomic distances are given in the literature. On the other hand, it is expected that the $-\frac{dq}{dr}$ -values do not deviate much from those calculated for the complex above.

5.4 Direct estimation of the charge parameter $\frac{dq}{dr}$.

An independent way to determine a value of $\frac{dq}{dr}$ is from experimentally determined charges on the nitrogen atoms and interatomic distances calculated from Badger's rule.⁷³ This rule has been used in the following form:

$$r_e = \left(\frac{c_{ij}}{k_e} \right)^{1/3} + d_{ij}$$

From this relation it is evident that the interatomic distance r_e depends only on the force constant k_e , since c_{ij} and d_{ij} are constants for the same i and j atoms of the periodic system. The force constants of the N-N bond in the dinitrogen complexes have been calculated from the expression¹⁸

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k_e}{\mu_{red}}}$$

The experimentally determined charges on the nitrogen atoms in the complexes of rhenium and iridium are then plotted against the N-N distance determined from Badger's rule. The $\frac{dq}{dr}$ -values obtained from the slopes of the straight lines depend of course on the method of charge calculation. Furthermore, the variation in charge on the nitrogen atoms from one complex to another is not so pronounced and thereby the error in the $\frac{dq}{dr}$ -values is large. On the other hand, an obvious difference in the $\frac{dq}{dr}$ -values has been found, when the terminal nitrogen atom carries the largest or the smallest negative charge, viz. $-\frac{dq}{dr} \approx 2 - 3$ a.u. and $-\frac{dq}{dr} \approx 0.5 - 1.0$ a.u., respectively.

In section 5.3, the combination of infrared intensity data with ESCA data was presented. The results can now be compared with the results of the combination of infrared frequencies with ESCA data to get an approximate value of the charge parameter $\frac{dq}{dr}$. This quantity gives more information about the electronic structure of a molecule by indicating the degree of mobility of charges over the bond in question.

5.5 Assignment of charge on the nitrogen atoms in the dinitrogen complexes.

There has been some doubt in deciding⁷⁴ which nitrogen atom that should carry which charge. That the two nitrogen atoms in the dinitrogen complexes have different charges is now well established by ESCA. In the first paper by Leigh et al.³¹ on ESCA measurements of two rhenium dinitrogen complexes, the smallest nitrogen 1s binding energy was assigned to the terminal nitrogen atom, which thus is the most negative one.

In the present work it is suggested that it should be possible to make an assignment through a combination of infrared data with ESCA data. In the first estimation of $\frac{dq}{dr}$ -values (section 5.3) there was only a small difference in $\frac{dq}{dr}$, when the terminal nitrogen atom carries the largest or the smallest negative charge. But a more obvious difference in the $\frac{dq}{dr}$ -values has been found in the direct estimation of $\frac{dq}{dr}$ (section 5.4). From the fact that the value $-\frac{dq}{dr} \approx 0.5 - 1.0$ a.u. is more in agreement with the values obtained from infrared intensity data, it has been concluded that the terminal nitrogen atom carries the smallest negative charge.

The same assignment has recently been proposed by Leigh et al.⁷⁵ for the following reasons. It was found that for the dinitrogen complexes of rhenium in which the metal atom had a higher formal oxidation state, the dinitrogen gave only a broad peak with a maximum very near the binding energy determined for the least negative nitrogen atom of the rhenium(I) dinitrogen complex. From measurements on analogous rhenium carbonyl complexes it was found that the oxygen 1s electron binding energy was very little changed upon oxidation from rhenium(I) to rhenium(III). This means, upon extrapolation to the dinitrogen complexes, that the terminal nitrogen atom is changed very little upon oxidation. Hence, the more negative nitrogen atom should be the internal one.

Such an assignment has also recently been suggested by Nefedov et al.⁷⁶ They point out that the interaction of metal d electrons with the unoccupied antibonding π -orbitals of the dinitrogen ligand should lead to accumulation of negative charge primarily on the atom directly bound to the metal.

5.6 Metal core electron spectra of the dinitrogen complexes.

Some metal core electron spectra on the dinitrogen complexes and on some other metal compounds of various formal oxidation states have been recorded. Thereby, it was possible to get an idea about the charge on the metal atom in the dinitrogen complexes. It was found that the metal atom in the dinitrogen complexes of rhenium and iridium carries a small positive charge, as the metal electron binding energies were close to those observed for the pure metals. On the other hand, it is expected that the π^* -acceptor ability of the dinitrogen ligand should cause a lower electron density around

the metal atom and consequently a higher binding energy and a more positive charge on the metal atom. It has been suggested that it could be the σ -donor and π -acceptor ability of the phosphine ligands that influences the charge on the metal atom. It is evident that the σ -donor ability can be the most pronounced and thus cause an increase of the electron density around the metal atom and reduce the positive charge caused by π -backbonding to the dinitrogen ligand.

In the iron dinitrogen complex (paper VI) the metal atom has a formal oxidation state of +2, but the measured metal binding energies indicate a low positive charge on the iron atom. The simple model that the binding energy of an atom depends only on the effective charge on the atom in question is not always quite adequate. The binding energy also depends on the potential originating from the effective charge of all the other atoms in a molecule. It is thus reasonable that the potential from especially the negative hydride ions in the dinitrogen complex causes a low binding energy at the metal atom and thereby a seemingly low positive charge.

The metal atom in the dinitrogen complexes of ruthenium and osmium was found to be considerably more positive than the metal atom in the other investigated dinitrogen complexes. This is also to be expected as the metal atom in these latter complexes is surrounded by strongly electronegative halide ions.

6. CONCLUDING REMARKS

The present investigation has shown

1. The utility of infrared intensity and ESCA measurements to get information about charge distribution in a metal dinitrogen complex. The combination of these two kinds of measurements seems to be able to provide increased knowledge about the electronic structure of molecules, since it has been possible to determine approximately the variation of charge with interatomic distance. Furthermore, it has been found that the results from intensity measurements are confirmed and strengthened by the ESCA results.
2. In relation to point 1 above, the question about which nitrogen atom that should carry which charge has been elucidated. Thus, it has been found that the inner nitrogen atom is the most negative one.
3. The electronic structure around the two nitrogen atoms is different, as they were found to have different charges. The question of homolytic and heterolytic splitting of a diatomic molecule, e.g. dinitrogen, is of major interest when considering its "activation". If the charge separation on the nitrogen atoms is considered as a beginning of a splitting, this splitting is both homolytic and heterolytic. Homolytic, since both the nitrogen atoms are negatively charged and heterolytic since there is a small difference in charge on the two nitrogen atoms.
4. The fact that both the nitrogen atoms in the dinitrogen complexes are negatively charged means that the electron transfer has gone from the metal atom to the dinitrogen ligand. As the donated

electrons occupy the antibonding π -orbitals of dinitrogen, this means that the two nitrogen atoms are bound together in something more like a double bond instead of a triple bond that exists in the not activated dinitrogen group. This is indicated by the reduction of the N-N stretching frequency.

5. The nucleophilic property of the dinitrogen group and the fact that the inner nitrogen atom is more nucleophilic than the terminal one.

It is my hope that the present results may be of use for resolving the important problem of reducing the dinitrogen group coordinated to metal complexes of similar type. This problem is connected with the catalytic production of ammonia, hydrazine or amines under, hopefully, mild conditions.

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